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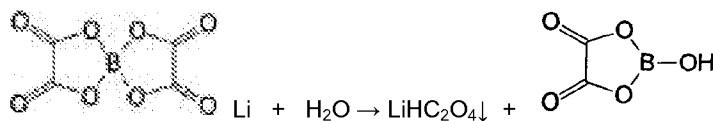
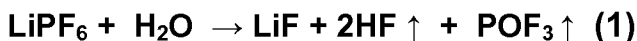
(54) Process to Dry Organic Liquid Electrolytes

(57) The patent describes a process to remove water and other protic contaminants from an organic liquid electrolyte, where the organic liquid electrolyte is brought into contact with one or more insoluble alkali metal hydride and the resulting insoluble byproducts of the reaction are separated out.

Description

[0001] The present invention concerns a process to remove water and other protic contaminants from organic liquid electrolytes.

[0002] Lithium batteries in use today (whether primary or secondary battery cells) normally contain electrolytes that are liquid, devoid of water, and that have ionic conductivity; such electrolytes contain conducting salts such as LiPF_6 , LiBF_4 , LiClO_4 , lithium imide, lithium methide or lithium chelate compounds such as lithium-bis(oxalato) borate in dissolved form. Many of these conducting salts dissolve more or less quickly in the presence of protic compounds, such as water, for example, as follows



(2) **[0003]** Gaseous products
(HF, POF_3 and others)

formed in the hydrolysis of conducting salts containing fluorine are highly corrosive and will damage the other battery components, such as the cathode materials. For example, HF will dissolve manganese spinelles and will damage the surface layer of the electrodes, which is so important for longevity. As a result, the cyclic stability of secondary batteries will be impacted detrimentally. Borate electrolytes are also sensitive to water. In this instance, insoluble hydrolysis products will be formed that will limit the functionality. Even though there are conducting salts, such as LiClO_4 , which are inert in water, the presence of water will lead to negative effects in this case as well, based primarily on interference with the formation of the surface layer and increased pressure due to the reaction with the anode in accordance with

$$\text{Li} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2 \uparrow \quad (3)$$

[0004] It is thus necessary to reduce the content of protic contaminants to a minimum ($\text{H}_2\text{O} < 20$ ppm, $\text{HF} < \text{roughly } 30$ ppm). A number of processes have been developed to accomplish this, but all of them have disadvantages.

[0005] JP 208 7473 proposes to mix electrolyte solutions with a solvent that forms azeotropic mixtures with a low boiling point in water and to remove the water / solvent azeotrope by distillation. The disadvantages of

this process are the undesirable contamination with the carrier solvent and the restriction to electrolyte solvents with a high boiling point.

[0006] US 5 395 486 and WO 2000038813 use inert fluorinated liquids, such as C_8F_{18} , as carriers. The disadvantage of these processes, among other disadvantages, relates to the associated emission of compounds containing fluorine.

[0007] The process proposed in JP 103 38653, namely to handle the drying of electrolyte solutions by injection of dry inert gases, has the disadvantage that very expensive (reprocessed) inert gas must be used and that high losses of solvents are incurred, or that the resulting solvent vapors must be condensed and reprocessed at great expense.

[0008] Another process, which is described in DE 198 27 631 and in a similar form in JP 2000058119, relies on the physical adsorption of water and HF on specially treated aluminum oxide. The disadvantage of the adsorption process is the costly pretreatment of the aluminum oxide (drying for 4 weeks in nitrogen flow at 400°C).

[0009] DE 198 27 630 describes a cleaning process for battery electrolytes that brings a solid capable of chemically adsorbing protic contaminants into contact with the electrolyte solution and then separating the solid out. Unfortunately, the polymer-fixed cleaners containing amines are expensive and also require pretreatment (such as four days drying in vacuum at 100°C).

[0010] Finally, processes are known to dry electrolyte solutions by means of alkali metals. For example, F. P. Dousek et al. (Chem. Listy (1973), 67 (4) 427-32) propose to pre-dry with Molsieb and then to undertake a final drying with a liquid K/Na compound. In an essentially analogous method, JP 01122566 proposes to clean electrolyte solutions by filtering them in a column filled with solid alkali metals. However, the use of alkali metals in contact with relatively reactive solvents is not without perils from a safety standpoint. Thus, it is known, for example, that tetrahydrofuran will be damaged by lithium metal at temperatures above roughly 100°C. Likewise, other alkali metals may react very violently with the solvents used in lithium battery electrolytes at slightly elevated temperatures.

[0011] Modern super capacitors may contain an organic electrolyte, normally the solution of an ammonium salt in an aprotic solvent with a high dielectric constant, such as acetonitrile or γ -butyrolactone. The ammonium salts normally contain perfluorinated anions such as PF_6^- or BF_4^- . They are electrochemically stable, weakly nucleophilic and are not deposited in the active electrodes.

[0012] This type of electrolyte must also have a low content of water (< 20 ppm). In order to achieve this, JP 11054378 and JP 11008163 propose to add adsorbing materials, such as inorganic oxides, for example aluminosilicates, to the electrolyte. These adsorbing materials will lower the water content and will thus improve reliability, safety and current characteristics.

[0013] The disadvantages of this process are the required pre-treatment of the adsorbing materials and also that the adsorbing materials remain in the completed capacitor, which reduces its specific storage capacity.

[0014] The present invention has the objective of avoiding the disadvantages of the state of the arts and to provide for a process to remove water and other protic contaminants from organic liquid electrolytes. Organic liquid electrolytes are defined to be solutions that contain lithium and/or ammonium salts with electrochemically stable anions in aprotic polarized organic solvents.

[0015] This process is intended to

- be generally applicable,
- preclude the generation of additional contamination,
- use commercially available drying materials without additional conditioning,
- be safe and
- lead to product solutions with water contents as low as < 20 ppm.

[0016] The objective is solved by a process to remove water and other protic contaminants from an organic liquid electrolyte, where the organic liquid electrolyte is brought into contact with one or more insoluble alkali metal hydride and where the thus resulting insoluble byproducts of the reaction are removed. Removal of water and other protic contaminants is defined here as the partial or total removal.

[0017] In particular, the preferred drying material, namely the binary hydrides of lithium (LiH) and sodium (NaH), are relatively cheap in quantity and are available in pure form. Even though they are totally insoluble in the aprotic solvents used in lithium batteries, it has been established that LiH, NaH and the other alkali metal hydrides KH, RbH and CsH are fast-acting with regard to drying and that they can lead to very low residual levels of protic contamination. In addition, the results indicated surprisingly that the hydritic drying materials are much more advantageous with regard to safety than the alkali metals by themselves. DSC measurements (differential scanning calorimetry, completed in a RADEX apparatus of Systag / Switzerland) using mixtures of LiH or Li metal and lithium-bis(oxalato) borate solutions as well as LiClO₄ and LiPF₆ solutions indicate that the onset of the dangerous and strongly exothermic decomposition reaction, expressed as the so-called ONSET temperature (T_{ONSET}), is significantly higher for hydrides (see Table 1).

Table 1

Thermic Decomposition of Electrolytes in Contact with LiH and Li Metal (Radex-Experiments)

EC = Ethylene carbonate, DMC = Dimethyl carbonate, PC = Propylene carbonate,

DME = 1,2-Dimethoxyethan, LOB = Lithium-bis(oxalato) borate

Electrolyte	Concentration of Conducting Salt (% by weight)	Li Metal T_{Onset}	Li Metal T_{Max}	LiH T_{Onset}	LiH T_{Max}
LiPF_6 / EC-DMC	11	145	160	230	(240) ¹
LiClO_4 /PC-DME	6	160	165	255	265
LOB / EC-DMC	10.5	180	220	240	./. ¹

¹ T_{Max} cannot be determined or only with difficulty, because the container burst.

T_{Onset} = Start of first exotherm (°C)

T_{Max} = Maximum of exotherm (°C)

[0018] The comparison data indicate that the hydrides will assure a high degree of worker safety, which is extremely important for production runs in large volume.

[0019] The process described in the invention can be applied to all organic liquid electrolytes, thus, for example, to solutions of:

Fluorides such as	MPF_6 , MAsF_6 , MBF_4
Perchlorates	MCl_4
Lithium iodide	LiI
Triflates	MSO_3R_F
Imides	$\text{MN}(\text{SO}_2\text{R}_F)_2$
Methides	$\text{M}[\text{C}(\text{SO}_2\text{R}_F)_3]$
Chelatoborates	$\text{M}[\text{L}_2\text{B}]$
Chelatophosphates	$\text{M}[\text{L}_3\text{P}]$

[0020] with $\text{M} = \text{Li}$ or NR_4 ($\text{R} = \text{H}$ or alkyl with 1-10 C atoms, also cyclical)

R_F = perfluorated alkyl rest with 1-10 C atoms, also cyclical)

L = two-pronged ligand with two O atoms, such as oxalate, catecholate, salicylate, also partly or completely fluoridated in aprotic solvents with high dielectric constant, such as:

Carbonates, such as dimethyl carbonate, diethyl carbonate, ethylene carbonate, propylene carbonate, ethylmethyl carbonate,

Nitriles, such as acetonitrile, adipic dinitrile, glutardinitrile

Lactones, such as γ -butyrolactone,

Amides, such as dimethyl formamide, N-methyl pyrrolidone,

Ethers, such as tetrahydrofuran, 2-methyltetrahydrofuran,

1,2-Dimethoxyethane (monoglyms), 1,3-dioxolane

Acetales, such as 1,1-diethoxymethane

Sulfur compounds, such as dimethyl sulfoxide, sulfolane and their mixtures.

[0021] The alkali metal reacts energetically and irreversibly with proton-active substances in accordance with:



X = HO, Halogen, RCOO, RO etc.

R = alkyl

[0022] The hydride is added to the liquid electrolyte stepwise in small amounts to keep the reaction (4), which produces gas, from turning excessively violent. A further preferable embodiment of the invention holds the content of proton-active substances, such as water, below a specified upper limit of 0.6 mmol/g active H concentration, such as 1% water. Liquid electrolytes with heavier contamination may be dried using the safety precautions known to the person skilled in the arts, but it is preferable to use another drying process first and to handle only the final drying step with the process of the invention.

[0023] The drying process of the invention can be carried out as described below.

[0024] The moist liquid electrolyte, which may be contaminated with other proton-active substances, is preferably mixed with an alkali metal hydride in small increments by stirring. This process occurs preferably at temperatures in the range of 0 to 150°C, particularly preferably 0 to 90°C. The drying process may be monitored easily by measurements of the gas volume that is generated. In some cases (mainly in the presence of significant amounts of acid, such as 0.1 mmol/g HCl), the generation of gas is very violent with foaming. Such instances require cooling. The reaction is essentially not noticeably exothermic in all other cases. Depending on the activity of the drying material, a post-reaction phase at room temperature or elevated temperature (as much as 90°C, in some instances to 120°C) may be required to complete the drying process.

[0025] The amount of drying material required depends on the "activity level" of the metal hydride used, on the one hand, and on the concentration of the proton-active contaminant, normally water, on the other hand. The water content is normally measured by a Karl Fischer titration (or an alternative method of determining water). In order to shorten the reaction time, the drying material may be used preferably in stoichiometric excess (such as 2 to 100 fold). The degree of excess in any particular instance depends on the activity level of the hydride and the specific performance of the drying operation. The drying potential depends here on the "active surface" of the metal hydride, specifically such that the effectiveness is improved for finer distribution degrees of the metal hydride. Moreover, the drying capacity of the metal hydride depends on the type of pre-treatment.

[0026] Generally, the "fresher" the metal hydride is, the more active it will be. Metal hydrides that are in contact with air or moisture are "passivated" and will normally need to be activated. This may be done by milling in an inert gas atmosphere. This process may be handled in a separate location or in situ, i.e. during the electrolyte drying process.

[0027] It has been shown that the hydride qualities on the market are sufficiently active to dry an electrolyte to a water content of < 20 ppm within a few hours. The drying process is aided by preferably stirring intensively, at the laboratory level with a fast propeller stirrer, for example. The drying process may also be undertaken such that the liquid electrolyte flows across a solid bed (such as a column) that contains the metal hydride.

[0028] Once the drying process is completed, the residues of the drying material and insoluble reaction products need to be separated out. It has been shown that the alkali metal hydride generated in accordance with (4) is totally insoluble in the solvents or mixtures of solvents listed above. Thus, the offending byproducts of the reaction may be removed by a simple separation of solid from liquid material, such as by filtration or centrifugation.

[0029] The clear solutions obtained in this manner have an extremely low water content (and also a low content of other proton-active substances). They may be used without further treatment as electrolytes for galvanic cells, preferably lithium batteries, or electrolytic double layer capacitors (super capacitors).

[0030] The object of the invention will be discussed in more detail in the following by reference to embodiment examples:

Examples 1 to 6 Drying of Various Electrolyte Solutions

[0031] Various electrolyte solutions, which are listed in Table 2, were dried under various drying conditions with the assistance of the process of the invention. The general experimental structure was as follows: The raw electrolyte solution in question was inserted into an inert multinecked flask that was equipped with a KPG stirrer, a mechanism for inserting solids and a heating element. A sample was removed by means of a plastic syringe, and the sample was analyzed for its water content by Karl Fischer titration.

[0032] The amount of LiH specified in Table 2 was added and stirred as specified in Table 2. After the drying period specified had passed, samples were again taken; they were filtered with syringe tip filters (such as Minisart SRP, 0.45 µm pore size, manufactured by Sartorius) and again analyzed for their water content.

[0033] The dried solutions were then filtered by glass filter frits.

Table 2
Drying conditions of Various Electrolytes

Sample	Electrolyte Solution	H ₂ O Content (ppm)	Amount (g)	LiH Amount (g)	Drying Temperature (°C)	Drying Period (hrs)	H ₂ O Content (ppm)
1	LiClO ₄ /PC-DME	870	150	0.8	room temp.	2.5	265
2	ditto	ditto	ditto	ditto	ditto	15	15
3	LiClO ₄ /PC-DME	340	8000	3.4	70	2	100
4	ditto	340	8000	4.7	70	5	10
5	LOB/PC-DME	340	1010	4.8	40	24	55
6	LOB/EC-DMC	120	2600	15.4	70	24	<20

[0034] As Table 2 indicates, the degree of drying depends on the conditions in each case. In order to obtain residual water contents of < 20 ppm, the examples shown require drying periods of 5 to 24 hours.

Patent Claims

1. A process to remove water and other protic contaminants from an organic liquid electrolyte, characterized by bringing the organic liquid electrolyte into contact with one or more insoluble alkali metal hydride and separating out the resulting insoluble byproducts of the reaction.
2. The process in accordance with Claim 1, characterized by using LiH and/or NaH as the alkali metal hydride.
3. The process in accordance with Claim 2, characterized by using only LiH as the alkali metal hydride.
4. The process in accordance with one of Claims 1 to 3, characterized by a content of protic compounds in the liquid electrolytes to be dried of < 0.6 mmol/g.
5. The process in accordance with one of Claims 1 to 4, characterized by temperatures of -20 to 150°C.
6. The process in accordance with Claim 5,

characterized by
temperatures of 0 to 90°C.

7. The process in accordance with one of Claims 1 to 6,
characterized by
amounts of metal hydrides equivalent to the stoichiometric amount of protic contaminants.

8. The process in accordance with Claim 7,
characterized by
an amount of metal hydride equivalent to 2 to 100 times the stoichiometric amount of protic contaminants.

9. The process in accordance with one of Claims 1 to 8,
characterized by
activating the metal hydride by milling under an inert gas atmosphere.

10. The process in accordance with one of Claims 1 to 9,
characterized by
stirring the liquid electrolyte with the metal hydride.

11. The process in accordance with one of Claims 1 to 9,
characterized by
running the liquid electrolyte over a solid bed containing the metal hydride.

12. The process in accordance with one of Claims 1 to 11,
characterized by
separating out the insoluble byproducts of the reaction by filtration or centrifugation.

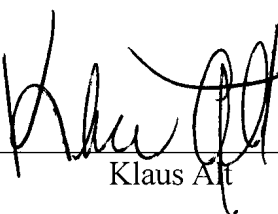
13. Use of organic liquid electrolytes dried in accordance with one of Claims 1 to 12 in galvanic cells or
super capacitors.

14. Use of organic liquid electrolytes dried in accordance with one of Claims 1 to 12 in lithium batteries.

Certification

This is to certify that the foregoing translation of the patent document entitled **“Process to Dry Organic Liquid Electrolytes”** was made from German to English by a competent translator well acquainted with both languages, and that, to the best of our knowledge and belief, it is a true and complete rendering into English of the original document.

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